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Title: PM_{2.5} Technology Assessment and Characterization Study in New York State (PMTACS-NY)

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Institution: Atmospheric Sciences Research Center, University at Albany

Research Category: Particulate Matter EPA "Supersites" Program

Sorting Code: 99-NCERQA-X1

Project Period: July - September 2001

Objective of Research:

As a result of recent clinical and epidemiological studies (NRC, 1998) associating adverse health effects in humans and fine particle mass, a new National Ambient Air Quality Standard for PM_{2.5} mass (15 $\mu\text{g}/\text{m}^3$ annual and 65 $\mu\text{g}/\text{m}^3$ 24-hr average) has been promulgated in the United States (Federal Register, 1997). Significant scientific and technical issues surrounding the mitigation of the warm season PM_{2.5} /co-pollutant complex and its interdependence with O₃ air quality through coupled photochemical pathways, common precursors, and similar dependencies upon meteorology must be addressed if effective control strategies are to be implemented.

The long-term monitoring of the PM_{2.5}/co-pollutant complex and its precursors at urban and regional representative sites provides the opportunity to track the impact of emission controls and their effectiveness on air quality. These data can be used to verify that implemented PM_{2.5} primary and secondary precursor (including ozone precursor) emission controls are performing according to specifications and verify that PM_{2.5} and ozone air quality has responded to the emission changes achieved as expected. Without adequate monitoring systems to track the progress and effectiveness of implemented control programs, the air quality management approach remains unaccountable.

The PMTACS-NY Supersite program provides a unique and unparalleled opportunity to enhance our understanding of ozone/PM_{2.5}-precursor relationships and track progress in current precursor emission control programs and assess their effectiveness in achieving expected air quality responses. The impact of this research is highly significant, providing a sound scientific basis for informed effective decisions in the management of air quality in New York and will benefit its citizens both environmentally and economically.

The PMTACS-NY is designed around three major objectives and addresses a series of science policy relevant questions related to hypotheses to be tested using measurement data collected under the program. The subject quarterly reports provide highlights on the overall program status, the progress made in the context of the specific tasks associated with the three program

objectives, identification of outstanding issues, project schedule and completion status by task, and a budget analysis.

Progress Summary/Accomplishments:

The PMTACS-NY 2001 Summer Intensive measurement program was operational on June 30, 2001. Approximately 85% of the measurements systems identified in PMTACS-NY network (Queens College/PS219, Pinnacle State Park, Whiteface Mountain) were online on the start date. During the six week Summer Intensive over sixty scientists participated in the measurement program (see <http://www.asrc.cestm.albany.edu/pmtacsny/local.htm> for details regarding the Summer Intensive). The summer program was a major success with very few glitches in field operations. We expect the measurement data set will address the three major objectives of the program and many of the scientific hypotheses posed.

Objective I. Measure the temporal and spatial distribution of the PM_{2.5}/co-Pollutant complex including: SO₂, CO, VOCs/Air Toxics, NO, NO₂, O₃, NO_y, H₂CO, HNO₃, HONO, PM_{2.5} (mass, SO₄⁻, NO₃⁻, OC, EC, Trace Elements), single particle aerosol composition, CN, OH and HO₂ to support regulatory requirements to develop cost effective mitigation strategies PM_{2.5} and its co-pollutants and to establish trends in the relevant precursor concentrations to assess the impact of recent and future emission reductions in terms of emission control effectiveness and air quality response.

Measurements at our two rural sites Whiteface Mountain and Pinnacle State Park operated during the quarter as outlined in Table 1 of the QAPP. Two of the NYSDEC urban sites Mabel Dean Bacon and IS 52 in the South Bronx had to be taken off line. In the case of Mabel Dean Bacon, the closure is permanent as a result of a major renovation that will add two stories to the building. In the case of the South Bronx, the school had to be closed for an asbestos abatement project that involved the floors containing our monitoring equipment. This site will be back online by September 6 and will remain as one of our core NYC sites.

Objective II. Monitor the effectiveness of new emission control technologies [i.e. Compressed Natural Gas (CNG) bus deployment and Continuously Regenerating Technology (CRT)] introduced in New York City and its impact on ambient air quality, thorough remote open path roadside, mobile platform, and fixed site measurements of CO₂, CO, NO, H₂CO, HONO, CN and aerosol chemical composition.

CEPEX implementation as part of the Summer 2001 Intensive Study was also quite successful. Over 150 vehicles were tracked and sampled, and several special event studies were also carried out. Some preliminary findings confirmed the NO₂ slip on CRT equipped diesels observed in the Fall 2000 feasibility study and formaldehyde measurements in the exhaust plumes of CNG buses were significant and will warrant further study.

Objective III. Test and evaluate new measurement technologies and provide tech-transfer of demonstrated operationally robust technologies for network operation in support of the development of process science and observation based analysis tools and health based exposure assessments.

Several data sets have undergone preliminary analysis in preparation for the Environmental Monitoring, Evaluation, and Protection in New York: Linking Science and Policy. NYSERDA Conference, September 24-25, 2001, Albany, NY. NYSERDA is a cost-sharing partner in the PMTACS-NY program. These initial evaluation studies include performance testing of the Rupprecht & Patashnick Co., Inc. (R&P) SES TEOM system and Series 8400N Ambient Particulate Nitrate Monitor. The abstracts from these presentations are attached. Posters for these sessions will be made available on the web.

Publications/Presentations: Demerjian, K.L., et al., “A comparison of urban and rural PM_{2.5} chemical species composition in New York State”, 222nd Annual ACS Fall National Meeting, August 26-31, 2001 Chicago, IL; Demerjian, K.L., et al., “New York Fine Particle Technology Assessment and Characterization Study”, Environmental Monitoring, Evaluation, and Protection in New York: Linking Science and Policy. NYSERDA Conference, September 24-25, 2001, Albany, NY.

Future Activities and Outstanding Issues:

During the next quarter we will prepare materials and participating in the EPA PM Supersites Program Meeting: Data Analysis Workshop & Planning for ESPO2, RTP, NC on November 13-14, 2001. In addition we will host the first PMTACS-NY data workshop on November 26-27 in Albany. At this meeting we have asked that each investigator give a 15-20 min presentation summarizing their data. This will include: period of operation, ~ % of valid data for the operation period, QA/QC checks performed, data snapshots (i.e. time series, summary statistics, etc.) of their measurements and any preliminary analyses they have considered to date. After we have heard from all investigators regarding their data, we will identify and discuss integrated data analysis tasks in response to the programs hypothesis and science objectives. We envision assigning team leaders and members for each relevant task identified. The science teams will be responsible to work up the necessary data and analyses to address the task and identify opportunities for manuscript preparation for dissemination of the results.

Supplemental Keywords: ambient air, atmospheric aerosols, ozone, particulate matter, metals, nitrogen oxides, sulfates, organics, atmospheric chemistry, monitoring, measurement methods, northeast air quality.

Relevant Web Sites: <http://www.asrc.cestm.albany.edu/pmtacsny/>

A COMPARISON OF URBAN AND RURAL PM_{2.5} CHEMICAL SPECIES COMPOSITION IN NEW YORK STATE

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Significant scientific and technical issues surrounding the mitigation of the PM_{2.5} /co-pollutant complex and the interdependence of photochemical and meteorological processes remain to be resolved, if effective control strategies are to be implemented. PM_{2.5}, like O₃, has a regional component that must be characterized to determine its source and role in the development of mitigation strategies for non-attainment areas. Chemical speciation measurements of PM_{2.5} at urban and regional representative sites are essential in support of analyses to help elucidate our understanding of: 1) the chemical and physical processes that couple urban and regional air quality; 2) the role that anthropogenic and biogenic sources of VOC, NO_x, SO₂ and primary particulate play in the production of the PM_{2.5}/co-pollutant complex in time (diurnal, seasonal, and inter annual) and space (local to regional); and 3) the effectiveness of emission control technologies on air quality. PM_{2.5} chemical speciation data collected in 2000 in New York City are compared with similar measurements made at a rural site in the Northeast. The implications of the compositional similarities and differences with regard to precursor concentrations and primary source contributions are discussed.

Abstract for NYSERDA Conference:
Environmental Monitoring, Evaluation, and Protection in New York: Linking Science and Policy
September 24-25, 2001

CONTINUOUS PM-2.5 SULFATE IN QUEENS, NY MEASURED USING FOUR DIFFERENT TECHNIQUES

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During the July 2001 NYC PM supersite intensive campaign at Queens College, we operated four different instruments capable of measuring the sulfate mass concentrations continuously in the ambient PM-2.5 aerosol. The four instruments were: 1) an Aerosol Mass Spectrometer (AMS) built by Aerodyne Research, Inc., and operated by ASRC; 2) a Particle Into Liquid Sampler (PILS) built by Georgia Tech and operated jointly by ASRC and Georgia Tech; 3) a Rupprecht and Patashnick 8400S Particulate Sulfate Monitor owned and operated by ASRC; and 4) a continuous sulfate monitor designed by Harvard School of Public Health and licensed, built and operated by ASRC. Each of these techniques will be described, along with the calibration procedures used to verify the data produced. Preliminary data from the July 2001 intensive study period will be presented. Early indications are that sulfate (as SO_4) reached levels near or above $20 \mu\text{g m}^{-3}$ for short periods during the study. As much as possible, data sets will be compared over the whole time period, and in more detail during high sulfate events. If filter data from the EPA speciation samplers is available, we will also compare the continuous and semi-continuous measurements with the 24-hour filter samples.

Abstract for NYSERDA Conference:

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**PM-2.5 MASS MEASUREMENT AT A RURAL NEW YORK STATE SITE:
COMPARISONS OF FRM FILTER BASED 24 HOUR MEASUREMENTS AND
CONTINUOUS TEOM MEASUREMENTS WITH AND WITHOUT A NAFION DRYER**

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The Federal Ambient Air Quality Standard for Fine Particulate Matter (PM-2.5) is based on 24-hour filter measurements. There is a large network of sites making and reporting these mass concentration measurements, both in New York, and across the country. Unfortunately, filter based measurements have known problems, most notably 1) loss of volatile species during long collection periods or shipment; and 2) inability to capture short duration, high concentration events. We will present comparisons of 24-hour Federal Reference Method (FRM) filter based measurements of PM-2.5 mass concentrations with PM-2.5 mass concentrations measured by a commercially available continuous Tapered Element Oscillating Microbalance (TEOM) analyzer. We have operated the FRM sampler and the standard TEOM (collection filter at 50 °C, no Nafion dryer) for just over two years, and the SES TEOM (collection filter at 30 °C, Nafion dryer in sample stream) for more than one year at our Pinnacle State Park site in Addison, NY. This site is in southwestern New York, south of the Finger Lakes, and about 10 miles southwest of Corning. We have recently added an EPA PM-2.5 chemical speciation sampler and an IMPROVE chemical speciation sampler at this site. If initial data from these samplers is available, we will also present comparisons of these measurements. Implications of these measurements for regional air quality will be discussed.

Abstract for NYSERDA Conference:

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**AEROSOL GENERATION AND CALIBRATION FACILITY
FOR AEROSOL RESEARCH AND THE EVALUATION OF
AEROSOL MEASURING TECHNIQUES AND INSTRUMENTATION**

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An aerosol generation and calibration facility was developed in the Atmospheric Science Research Center. In this facility, aerosols of known size and composition and concentration are generated, subjected to a well-characterized environment, and then used for calibration of aerosol measuring instruments, for evaluation of the performance of various commercial and research aerosol instruments.

Generated particles include organic and inorganic aerosols, as well as aerosols of mixed composition. Small aerosol particles (0.02 micrometers - 1 micrometer size range) are generated by spray atomization of aqueous and non-aqueous solutions or suspensions. Monodispersed aerosol is produced by further mobility classification of the polydispersed aerosol. Larger monodispersed aerosols (0.5 micrometer - 20 micrometer size range) are generated using a vibrating orifice technique.

Generated aerosols are delivered to a slow-flow chamber under controlled temperature, humidity and dilution flow conditions, allowing control of concentration levels and particle residence time in the chamber. These aerosols are used to challenge ambient particulate matter mass and chemical species monitors and evaluate their performance.

In addition, generated calibration and test aerosols are also delivered directly or by way of a static chamber to challenge particle sizing and number counting instrumentation and evaluate their performance.

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THE MEASUREMENT OF NO_y AT WHITEFACE MOUNTAIN: SAMPLING ISSUES AND THE EFFECT OF CLOUD WATER

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The continuous year around measurement of NO_y at Whiteface Mountain requires addressing several operational issues unique to this observational facility. These specifically concern the impact of cloud water on the NO_y molybdenum (moly) catalytic converter and its degradation and the determination of NO_y line losses during winter operations when it is not practical to operate the NO_y catalytic converter outside.

This presentation provides experimental evidence indicating that sustained exposures of NO_y moly converter to cloud water, alters its conversion efficiencies and leads to its rapid degradation, making routine NO_y observations impractical. In addition, liquid water in the sampling line or the reaction chamber can give rise to spurious detection noise during cloud events introducing significant measurement errors. An automated sampling system that allows discrimination of in-cloud days has been designed and implemented and results reported. Experimental studies of line losses based on the simultaneous operation of two NO_y measurement systems, one with the moly converter inside summit building next to the NO_x detector and the other with the moly converter placed outside (recommended configuration) on the summit roof. The results indicate significant line losses of NO_y constituents, (most likely HNO₃) in the former configuration consistent with previous studies, but also indicate that line losses during winter periods are significantly less than that observed during summer time periods.

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